Letters to the Editor

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SOME CONSEQUENCES OF CARATHEODORY'S PRINCIPLE IN AXIOMATIC THERMODYNAMICS

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In axiomatic development of thermodynamics after Carathéodory (1909), thermodynamic states of a simple system are specified by a point in an $(n+1)$-dimensional space of which, n co-ordinates, $x_1, x_2, \ldots, x_n$ are mechanically controllable, i.e., admit arbitrary variations by mechanical means and the other, x_0, is to take into account non-mechanical experiences. After Carathéodory the first principle may be formulated as "for every adiabatic change of states, if U and $\bar{U}$ are the initial and final values of internal energy and A the external work done

$$\bar{U}-U+A=0"$$

This may be looked upon, as mathematical characterisation of adiabatic processes by the internal energy of the system. The second principle, generally referred to as Caratheodory's principle, "in an arbitrary neighbourhood of every point, P, in the state-space, there exists a point inaccessible adiabatically from P". In conformity with the general continuity principle of macroscopic physics, thermodynamic functions including U and its first derivatives are continuous functions.

For applying this principle in thermodynamics, Carathéodory further assumed that $\dfrac{\partial U}{\partial x_0} \neq 0$ except for a few points. The same was taken by T. Ehrenfest-Afanassjewa as one of many additional but independent elementary axioms, introduced in her paper (1925).

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The object of the present analysis is to show that the fact $\frac{\partial U}{\partial x_0} \neq 0$ is a direct consequence of Carathéodory's principle. It is also pointed out how it is connected with the temperature axiom of T. Ehrenfest-Afanassjewa, introduced by her as an independent axiom.

The first principle for adiabatic transformations in the neighbourhood of a state, P, is

$$dU + \sum_{i=1}^{n} X_i dx_i = 0 \quad \ldots \quad (1)$$

where X_i's are generalised thermodynamic forces corresponding to x_i's, and taken as measurable. It can be re-written as

$$\frac{\partial U}{\partial x_0} dx_0 + \sum_{i=1}^{n} X_i' dx_i \quad \ldots \quad (2)$$

where
$$X_i' = X_i + \frac{\partial U}{\partial x_i}$$

Proposition : In equation (2), $\frac{\partial U}{\partial x_0}$ can never be zero.

Proof : If possible, let $\frac{\partial U}{\partial x_0} = 0$

Then
$$\sum_{i=1}^{n} X_i' dx_i = 0.$$

As dx_i's are arbitrary variations of controllable variables, so

$$X_i' = 0 \qquad i = 1, 2, 3, \ldots$$

Thus in the neighbourhood of P, the equation (2) becomes an identity, i.e., is satisfied by all points. It contradicts Carathéodory's principle. Then follows the proposition.

According to the general principle of continuity, $\frac{\partial U}{\partial x_0}$ being continuous, can not change the sign without passing through zero. Thus we get

Corrollary : $\frac{\partial U}{\partial x_0}$ must be of the same sign in all thermodynamic states.

Concluding Remark : In the developments after Carathéodory and others, $\frac{\partial U}{\partial x_0}$ is correlated (barring some factors) to the temperature. So, the above corrollary leads to the temperature axiom of T. Ehrenfest-Afanassjewa, viz., 'the temperature should be of the same sign'. The consequences of the Carathéodory's principle have not been fully explored. Some recent investigations have already been reported (Dutta, 1968).

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